

AD-A154 648

DTIC FILE COPY

UNCLASSIFIED  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
REPORT NUMBER ARO 15104.14-MS	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
TITLE (and Subtitle) Electrodeposition of Chromium and Copper in Magnetic Fields		5. TYPE OF REPORT & PERIOD COVERED 1 July 1981 - 31 Dec 1984 Final Report
AUTHOR(s) John Dash		6. PERFORMING ORG. REPORT NUMBER
PERFORMING ORGANIZATION NAME AND ADDRESS Portland State University Portland, OR 97207		8. CONTRACT OR GRANT NUMBER(s) DAAG29-81-C-0027
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE Feb 85
		13. NUMBER OF PAGES 5
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrodeposition Chromium Copper Magnetic fields		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Research had demonstrated several significant effects caused by the application of magnetic fields during electrolytic thinning and electrodeposition of metals. The purpose of the research supported by this contract was to continue studies of these effects. Research sought to determine what applied magnetic field strength and other parameters of electrolysis would maximize the following effects:		

DTIC  
ELECTE  
JUN 5 1985  
S E D

(a) Improvement in the uniformity of both anode and cathode processes. There is a natural tendency for much higher electric fields, and therefore, higher rates of electrolytic reactions at edges and asperities than at other points on the electrodes. Because the Hall effect is greatest where the electric field is greatest, a magnetic field improves uniformity of electrode processes.

(c) Inhibition of hydrogen gas formation during electrodeposition. Because of their higher mobility, the Hall effect on hydrogen ions is expected to be greater than on metal ions. This is expected to decrease the supply of hydrogen ions at the cathode and thus suppress hydrogen gas formation.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist.	Avail and/or Special
A/1	



Electrodeposition of Chromium and Copper

in Magnetic Fields  
Final Report  
John Dash

2-28-85

U.S. Army Research Office

Portland State University

Portland, OR 97207

Approved for Public Release;

Distribution Unlimited

### A. Statement of the problem studied.

Our previous research had demonstrated several significant effects caused by the application of magnetic fields during electrolytic thinning and electrodeposition of metals. The purpose of the research supported by this contract was to continue studies of these effects. We sought to determine what applied magnetic field strength and other parameters of electrolysis would maximize the following effects:

- (a) Improvement in the uniformity of both anode and cathode processes. There is a natural tendency for much higher electric fields, and therefore, higher rates of electrolytic reactions at edges and asperities than at other points on the electrodes. Because the Hall effect is greatest where the electric field is greatest, a magnetic field improves uniformity of electrode processes.
- (b) Increase in the speed of electrodeposition. Depletion of metal ions in the layer of electrolyte adjacent to the cathode normally limits the rate of electrodeposition of metals. The Lorentz force causes intense stirring in this layer, thus permitting replenishment of the metal ions and increase in the speed of deposition.
- (c) Inhibition of hydrogen gas formation during electrodeposition. Because of their higher mobility, the Hall effect on hydrogen ions is expected to be greater than on metal ions. This is expected to decrease the supply of hydrogen ions at the cathode and thus suppress hydrogen gas formation.

An additional goal of this research was to determine effects of magnetic fields on the properties of metallic deposits.

### B. Summary of the most important results

(a) To determine effects on uniformity and speed of deposition and on properties of the deposits, copper electrodeposition from copper sulphate solutions in magnetic fields was studied. It was found that compact copper deposits can be made at a current density of  $0.32 \text{ A/cm}^2$  in a magnetic field of 7 kG. The literature indicates that this current density is comparable with that which can produce compact deposits by employing high speed solution flow together with a spinning cathode. Very large or very small crystalline deposits can be produced, depending on the current density and the applied magnetic field. For example, with current density of  $0.08 \text{ A/cm}^2$  and 10 kG, the substrate crystals grow epitaxially into the deposit, and the deposit hardness is the same as the substrate hardness. By increasing current density to  $0.16 \text{ A/cm}^2$  with the same magnetic field strength, the deposit is smoother, crystal size of the deposit is too small to be detected with the light microscope, and deposit hardness is about twice that of the substrate. Periodic effects seem to occur. For example, at

fixed current density, increasing the magnetic field strength produces deposits with smaller and smaller crystals, until a certain minimum size (not yet measured) is produced. Further increases in magnetic field strength cause increase in grain size of the deposits. These results suggest the possibility of producing deposit microstructures ranging from single crystal to amorphous.

Recently,  $\text{Al}_2\text{O}_3$  particles have been co-deposited with copper from a  $\text{CuSO}_4$  solution. The  $\text{Al}_2\text{O}_3$  particles placed in the  $\text{CuSO}_4$  solution settle to the bottom of the container. These particles remain undisturbed at the bottom of the container with a DC current applied. However, the particles disperse throughout the solution and co-deposit with copper when the magnetic field is turned on. Results of preliminary experiments are promising. For example, it is possible to co-deposit either alpha or gamma  $\text{Al}_2\text{O}_3$  with copper in an applied magnetic field. The literature states that only alpha  $\text{Al}_2\text{O}_3$  can be co-deposited with copper when mechanical stirring is employed to suspend the  $\text{Al}_2\text{O}_3$  particles in the electrolyte.

(b) To determine effects on hydrogen gas formation, chromium electrodeposition from chromic acid solutions was studied. The maximum suppression of hydrogen gas formation by an applied magnetic field was found to be about 10%. This suppression was attributed to lowering of the cathode temperature due to intense stirring at the interface. The greater Hall effect on hydrogen ions does not seem to be a factor in hydrogen gas suppression.

During the course of these experiments, it was accidentally discovered that a small amount of methanol added to the chromic acid electrolyte causes an increase of about 20% in the current efficiency of chromium deposition. With further research it was determined that large concentrations of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  in the chromic acid solution at pH of about 1.6 results in deposition of chromium-iron alloys at current efficiencies of about 60% compared with about 20% for the conventional process. Deposits made at 60% current efficiency contain about one-half as much hydrogen as those made by the conventional process.

A presentation on this research was made at the ARO-sponsored Protective Coatings Workshop (Charleston, South Carolina, Dec. 13-16, 1982). The questioning afterward indicated that at least several scientists present did not believe that magnetic fields could significantly affect electrolysis. Subsequently, we produced a motion picture film to show the effects of magnetic fields on the bulk electrolyte and on gases formed at the electrodes. This film has been well-received at scientific meetings, and our results are no longer met with skepticism (at least not the vocal type).

## C. List of publications.

1. "Effect of Magnetic Fields on the Structure of Electro-deposited Copper", Proc. 38th Annual Meeting of EMSA, San Francisco, 1980 (Baton Rouge, Claitor's Publishing Div.) p. 144, with K. Housen.
2. "Use of AS1 for Increasing the Current Efficiency of Chromium Plating", Invention Report, PSU 1980, with A. Kasaaian.
3. "Radiation Emitted from a TEM due to an Air Leak", Bulletin EMSA 11, No. 2, 66 (1981), with B. McLaughlin.
4. "Improving Efficiency of Cr Plating with Higher Sulfate and Cr (III)", AES 69th Annual Technical Conference Proceedings, vol. 2, paper U4, San Francisco, June 1982, with A. Kasaaian.
5. "Use of Alcohol for Increasing the Current Efficiency of Chromium Plating", U.S. Patent No. 4,447,299, with A. Kasaaian. Application also filed for Canadian patent.
6. "Influence of Magnetic Fields on the Electrodeposition of Chromium", AES 70th Annual Technical Conference Proceedings, vol. 1, paper A4, Indianapolis, June 1983, with Ru-Tsin Chen and K. Housen.
7. "Effect of Magnetic Fields on the Morphology of Electro-deposited Copper," Proc. 41st Annual Meeting of EMSA, Phoenix, 1983 (San Francisco Press), with H. Takeo and S. Mal.
8. "Effects of Magnetic Fields and Flow Applied to Single Electrodes on Electrolytic Cell Potentials," J. Applied Phys. 55, 2604 (1984), with M. Takeo.
9. "The Effect of Magnetic Fields Applied during Aqueous Electrolysis on Circulation and on Electrode Processes," J. Appl. Phys. 55 2606 (1984), with C. Cousins and C. Gorg.
10. "Magnetic Effects on Electroplating of Copper," Proc. AES 11th Plating in the Electronics Industry Symposium, Orlando, Feb. 1984. With H. Takeo and C. Tam.
11. "High Efficiency Chromium and Chromium-Iron Plating", AES 71st Annual Technical Conf. Proc., N.Y., July 1984, with A. Kasaaian.
12. "SEM and EDS Study of Magnetic Effects on Electroplating of Cr-Fe Alloys," Proc. 42nd Annual Meeting of Electron Microscopy Society of America (San Francisco Press, 1984) p. 502. with C. Cousins.
13. Film: "Effects of Magnetic Fields on Aqueous Electrolysis", with C. Cousins and C. Gorg. June 1983.
14. "Use of Alcohol for Increasing the Current Efficiency and Quality of Chromium-Iron Alloy Plating", Patent Application filed in Great Britain and France. With A. Kasaaian.
15. "Chromium-Iron Alloy Plating Using Hexavalent and Trivalent Chromium Ion Solutions", U.S. Patent Application. With A. Kasaaian.

16. "Effect of Methanol and Formic Acid on Chromium Plating", Plating and Surface Finishing, 71, No. 11, p. 66 (Nov. 1984). With A. Kasaaian.
17. "Effects of Chromium Electroplating Solution Composition on Properties of the Deposits", AES 72nd Annual Technical Conf. Proc., Detroit, July 1985. With A. Kasaaian and W. Lanford.

D. List of participating scientific personnel

John Dash, Principal Investigator

Toshio Sahashi, Visiting Professor from Daido Institute of Technology, Nagoya, Japan

Fred Brace, Research Assistant

Robert Schiffman, Research Associate

David Roe, consultant

Makoto Takeo, consultant

Doug Collins, Research Assistant

Hiroshi Takeo, Research Assistant, MS., Physics (expected June 1985)

Arash Kasaaian, Ph.D., Physics, March 1985

N. Nguyen, Research Assistant

C. Cousins, Research Assistant, M.S., Physics, Dec. 1982

H. Mendoza, Research Assistant

C. Tam, Research Assistant